

LOW-PRESSURE SUBLIMATION METHOD FOR CESIUM DECONTAMINATION OF CLAY MINERALS

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ABSTRACT

We propose a low-pressure sublimation method as a new dry method to remove radioactive Cs from clay minerals. To develop this method, we used thermogravimetric analysis (TGA), thermal desorption spectroscopy (TDS), and X-ray photoelectron spectroscopy (XPS) to study Fukushima vermiculite particles saturated and sorbed with nonradioactive Cs and heated in air and under low-pressure and high-vacuum conditions. The results of low-pressure TGA show a mass decrease due to Cs desorption, which is not observed for TGA conducted with the samples in air. The Cs desorption peak at 680°C is confirmed by high-vacuum TDS. XPS measurements clarify that, on maintaining the samples at 800°C for 3 min in high vacuum, approximately 40% of the Cs desorbs from the vermiculite. Furthermore, TDS results show that adding a mixed salt, NaCl-CaCl₂, shifts the Cs desorption peak by 180°C to lower temperatures. These results demonstrate that the proposed method of low-pressure sublimation with added salts enables Cs decontamination of clay minerals at considerably lower temperatures than those in conventional dry methods.

Key words: Low-pressure sublimation, cesium, vermiculite, thermal desorption spectroscopy, X-ray photoelectron spectroscopy, thermogravimetry

INTRODUCTION

Three and a half years after the Fukushima Daiichi nuclear accident in 2011, ¹³⁷Cs, which has a 30-year half-life, has become the dominant radioactive contaminant. Most environmental ¹³⁷Cs occurs in clay minerals in the soil, which are very difficult to decontaminate. Several studies focused on the interaction between Cs and clay minerals and proposed models involving adsorption to the siloxane ditrigonal cavity and to the frayed-edge site (Sawhney, 1971; Kogure et al., 2012; Yamaguchi et al., 2012). Cs ions are more strongly fixed in mica-group clay minerals and smectite than other cations (Sawhney, 1965; Tamura and Jacobs, 1960), and irreversible sorption is also reported (Comans et al., 1990). Although ion exchange constitutes a general method for Cs removal from clay minerals, only a few tens of percent of Cs are typically extracted by this method. (Schulz, 1959). Thus, a new decontamination method is required.

Wet methods are often used to remove ¹³⁷Cs from clay minerals, such as ion exchange or a wet method involving acid solutions (Tsumura et al., 1984; Suzuki et al., 2013; Kobayashi et al., 2013). From among the many acids, oxalic acid is particularly effective for removing ¹³⁷Cs because it removes over 90% of the Cs (Suzuki et al., 2013). However, a drawback of this method is that the elution of Fe and Mn due to the strong chelate property of oxalic acid breaks the framework of the clay minerals, thereby degrading the properties of these materials (Shuman, 1982). Furthermore, according to a report by Kobayashi et al. (2013), treatment by oxalic acid does not remove Cs from certain clay minerals. For these reasons, an effective wet method for Cs decontamination of clay minerals is under development.

Dry methods, which constitute another approach to Cs decontamination, are infrequently employed. These methods involve heating clay minerals and filtering out the desorbed ¹³⁷Cs. Two advantages of dry methods are the absence of radioactive liquid wastes and reduced waste volume due to incineration. However, dry methods also have some disadvantages, one of which is that the framework of clay minerals can be broken as in the case of acid treatment. Studies based on differential thermal analysis report that many clay min-

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erals have endothermic peaks in the range of 750 to 1000°C originating from atomic rearrangements and recrystallization accompanied by decomposition (Földvári, 2011). Therefore, dry methods should be applied at the lowest possible temperatures. Another problem is that, when using only heat treatment, the Cs removal efficiency is small. For heating at 1300°C, no significant volatilization of Cs occurs (Takizawa et al., 2011). The structural phase transition of clay minerals that occurs at high temperatures is considered to cause the formation of stable silicate compounds such as CsAlSiO_4 , which is essentially not subtracted. Another study reports that Cs becomes more fixed in the soil upon heating from 100 to 600°C for 1 h (Ikegami et al., 2013). Addition of certain reaction accelerants has been proposed to resolve this problem. Spalding (1994) reports that more than 99% of Cs is removed from contaminated soil by heating to over 1000°C, and using NaCl and CaCO_3 as reaction accelerants. After 2011, some institutes and companies in Japan started developing dry methods (Honma et al., 2014; Minehara et al., 2013; Halada and Kato, 2014). Halada and Kato (2014) reported Cs removal at 700°C with NaCl and CaCl_2 as additives. However, low-temperature dry methods that do not lead to the decomposition of clay minerals are still under development.

To contribute to this development, we propose, herein, a low-pressure sublimation method. This method allows Cs removal at a lower temperature because Cs is prone to sublimate under low pressures. Although conventional dry methods for Cs decontamination have been applied under ambient atmosphere conditions, no report exists of dry methods applied under vacuum or low-pressure conditions. Thus, in the present study, we heated clay minerals saturated and sorbed with non-radioactive ^{133}Cs under low-pressure conditions and studied the enhancement of Cs desorption.

Although conventional dry methods frequently use radioactivity to assess the amount of residual Cs in soil, desorbed Cs is rarely monitored. In this study, we directly detect Cs by using thermal desorption spectroscopy (TDS) combined with a quadrupole mass spectrometer (QMS). Additionally, we use thermogravimetric analysis (TGA) to compare Cs desorption under atmospheric and low-pressure conditions. Finally, we use X-ray photoelectron spectroscopy (XPS) to quantitatively analyze the residual Cs in clay minerals. Because vermiculite fixes Cs better than other clay minerals [e.g., montmorillonite and kaolinite (Schulz et al., 1959)], we study vermiculite collected from Fukushima. Furthermore, we observe that using NaCl and CaCl_2 as reaction accelerants reduces the treatment temperature to less than 650°C.

EXPERIMENTAL

For this study, we used vermiculite collected from Onomachi, Fukushima Prefecture. Vermiculite particles were classified by elutriation (Handbook of Clays and Clay Minerals, 3rd edition). The particles ranged in size from 1.2 to 1.8 μm , as measured by dynamic light-scattering photometry (Ohtsuka Denshi, DLS8000). The classified vermiculite particles were stirred in a 5 mM water solution of nonradioactive CsCl (Wako, special grade) for 24 h. This operation was performed several times so that the particles were saturated with Cs. To remove

excess CsCl from the vermiculite suspension, a centrifuged deposit of vermiculite was dispersed in ethanol and centrifuged again. After several iterations of this procedure, negligible CsCl was confirmed by adding silver nitrate solution and verifying that the suspension was free of white turbidity. To estimate the Cs content, Cs-saturated vermiculite particles were dried at room temperature and analyzed by wavelength dispersive X-ray fluorescence spectrometry (Rigaku, ZSX Primus II); the resulting Cs content was 4.7 wt%. As a reference sample, K-saturated vermiculite particles were also formed with KCl (Kanto Kagaku, special grade).

Using a thermogravimetric (TG) analyzer, Cs- and K-saturated vermiculites were analyzed (Netzsch Japan, TG-DTA2010SE) in air and under low-pressure conditions. In a Pt pan, 15 to 20 mg vermiculite samples were heated to 900°C at a constant rate of 0.5°C/s. An empty Pt pan was placed on the reference balance. Low-pressure TG data were acquired with the balance chamber under dynamic vacuum (primary rotary pump followed by turbomolecular pump). The base pressure of the balance chamber was ~ 10 Pa, as measured by a crystal gauge (Canon Anelva, M-320XG) installed above the balance. The temperature was calibrated on the basis of the melting point of aluminum (660.3°C).

The TDS experiments were conducted with the samples in a high-vacuum chamber (base pressure of 2×10^{-6} Pa). Figure 1 shows a schematic illustration of the TDS apparatus. A 5 cc alumina crucible with an ~ 10 mg sample of vermiculite was heated to 800°C at a constant rate of 0.5°C/s by a tungsten heater installed in the vacuum chamber. The sample temperature was monitored with a K-type thermocouple placed in contact with the bottom of the crucible. In Fig. 1, the Cs beam desorbed from the sample is depicted by the dashed arrow. Desorbed species were detected by a QMS (Pfeiffer Vacuum, Prisma Plus QMG220M3) that orthogonally intercepted the Cs beam. A 3.4-mm-diameter aperture above the crucible allowed us to minimize contamination of the QMS to the lowest

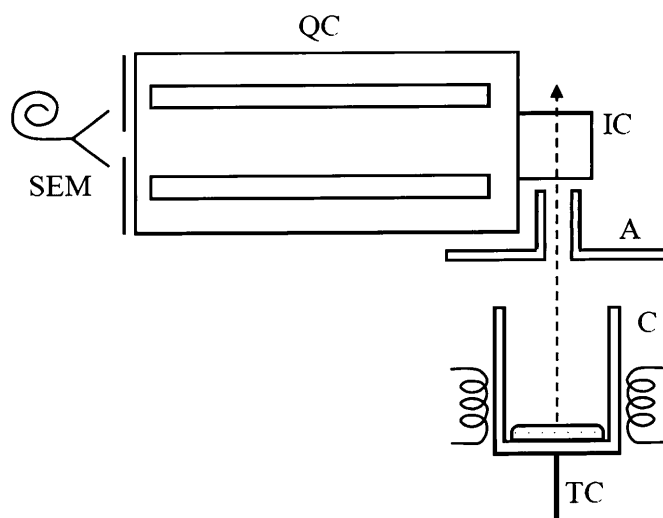


FIG. 1. Schematic illustration of TDS system. TC, C, A, IC, QC, and SEM denote K thermocouple, alumina crucible, aperture, ionization chamber, quadrupole chamber, and secondary electron multiplier, respectively. Dashed arrow shows the path of desorbed species from the sample, which is held in the crucible.

extent possible. Some desorbed species were ionized by the 80 eV electron beam in the ionization chamber and were detected by a secondary electron multiplier after mass separation in the quadrupole chamber. The ionization chamber was separated from the crucible by approximately 100 mm. After cooling to room temperature, the TDS background curve was measured by heating the crucible to 800°C at the same constant rate.

To estimate the amount of residual Cs in the vermiculite after the vacuum heat treatment, we conducted XPS measurements at the BL27A beamline of the Photon Factory of the High Energy Accelerator Research Organization (KEK-PF). The pellet samples used for XPS measurements were prepared by applying 0.29 GPa to Cs-saturated vermiculite on a 0.5-mm-thick Mo substrate for 30 min. Pellet samples on Mo substrates were introduced into an ultrahigh vacuum (UHV) chamber and X-ray photoelectron (XP) spectra of Cs $3d_{3/2}$ and Si $1s$ electrons were acquired prior to heating using a semispherical analyzer (VSW, Class100). The base pressure of the UHV chamber was approximately 1×10^{-7} Pa. Samples were heated to 400, 600, and 800°C at a constant rate of 25°C/min by irradiating the pellets with the 1064 nm line of a YAG laser (IB laser, cwQ-300). The various pellets were heated to different temperatures in vacuum, and these temperatures were maintained for approximately 3 min. A pyrometer (LEC, IGA250/2000) was used to measure the temperature. To avoid scattered YAG laser light from irradiating the pyrometer, we measured the temperature of the Mo substrate on the backside of the pellets. After cooling to room temperature, Cs $3d_{3/2}$ and Si $1s$ XP spectra were again acquired. A 3 keV monochromatic X-ray beam from BL27A was used as the X-ray source for the XPS measurements.

We also applied TDS to samples, with NaCl (Kishida Chemical, special grade) and CaCl₂ (Kishida Chemical, special grade) added as reaction accelerants. These salts were chosen on the basis of the report by Halada and Kato (2014). A 35 mM water solution of NaCl-CaCl₂ mixed salts with a 1/1 molar ratio was prepared and added to the Cs-saturated vermiculite, controlling the weight ratio of the mixed salt and vermiculite. The samples with added salt were dried in air.

To estimate the amount of residual Cs in the samples after low-pressure heat treatments with added NaCl-CaCl₂ mixed salt, XPS measurements were conducted with a sector-type analyzer (VG, CLAM2) and by using an Al $K\alpha$ source. First, we measured the Cs $3d$ and Si $2p$ XP spectra of salt-free Cs-saturated vermiculite fixed to a carbon tape. Next, 100 mg of Cs-saturated vermiculite powders were suspended in a 300 mM, 3.2 ml solution of NaCl-CaCl₂ mixed salt in water. The molar ratio of NaCl-CaCl₂ in this solution was 1/2. An alumina pan was filled with this suspension, which was dried in air at 90°C for approximately 2 h. With this procedure, we formed 20 mg solid samples, which were heated at a constant rate of 0.5°C/s to 650°C under low-pressure conditions (14 Pa). The samples were maintained at 650°C for 30 min. This low-pressure heat treatment was performed with the TG apparatus. After heating, the samples were dispersed by sonication in 10 mL of distilled water, and then centrifuged at 4000 rpm for 30 min. The centrifuge deposit was dried in air, and XP spectra were acquired from the dried sample fixed to carbon tape.

RESULTS AND DISCUSSION

Figure 2 shows TG curves of Cs-saturated vermiculite. The black and gray curves correspond to TG and its differential curve (DTG), respectively. The top and bottom panels correspond to the results obtained in air and under low-pressure (14 Pa) conditions, respectively. The vertical axis shows the weight decrease ratio as a percent of the initial weight (i.e., before heating). With the sample in air, two large decreases in weight occur: one at 50°C and one at 480°C. According to Földvári (2011), the dehydration reaction in vermiculite occurs in the following order: (1) below 200°C, water adsorbed on the surface is desorbed, (2) desorption of water sorbed in the interlayers, (3) from 250 to 300°C, the water bonds desorb from the interlayer cations, and (4) from 450 to 850°C, the hydroxyl groups are desorbed. Thus, we attribute the weight decreases at 50 and 480°C to processes (1) and (4), respectively. Because Cs has a small hydration energy, ion exchange from hydrated Mg²⁺ to Cs⁺ in vermiculite induces collapse and dehydration from the interlayers (Sawhney, 1971). Therefore, that processes (2) and (3) are not observed in the top panel of Fig. 2 is attributed to the loss of interlayer water induced by Cs sorption. However, the small dips from 250 to 300°C in the DTG curve may be attributed to processes (2) and (3).

Conversely, the low-pressure DTG curve differs from that obtained in air. First, the drop in the weight ratio due to water desorption around 50°C decreases, which we attribute to

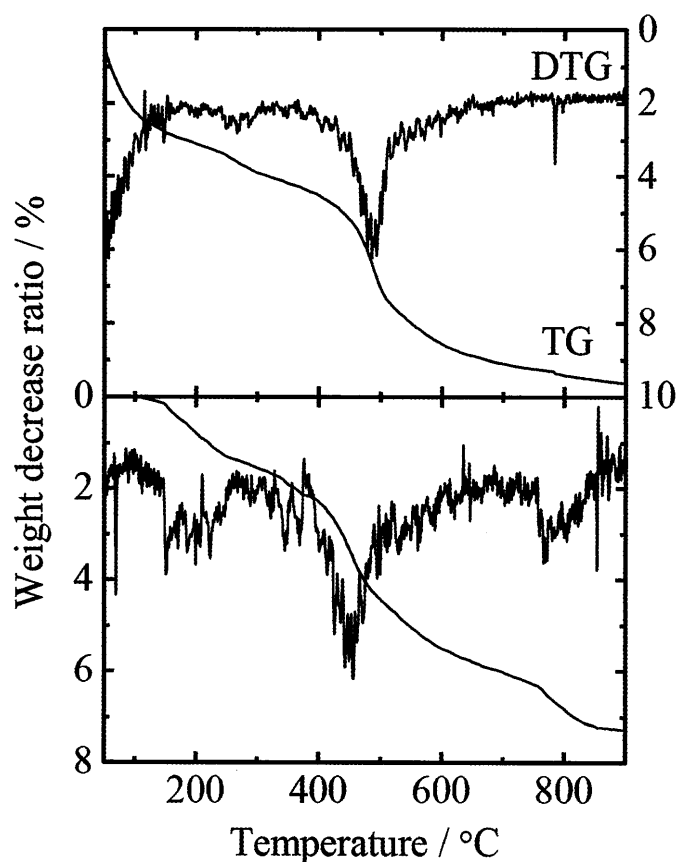


Fig. 2. TG and DTG curves of Cs-saturated vermiculite. Top and bottom panels correspond to the results obtained with the samples in air and under low-pressure conditions (14 Pa).

enhanced water desorption from surfaces at room temperature under low-pressure conditions. Second, clear multiple dips appear between 150 and 250°C. These dips originate from processes (2) and (3). The drop in the weight ratio due to desorption of the hydroxyl group also shifts by approximately 30°C to lower temperatures. These changes indicate that, in clay minerals, the dehydration reaction is facilitated under low-pressure conditions.

A similar tendency is also observed for K-saturated vermiculite. Figure 3 shows TG and DTG curves for K-saturated vermiculite. The top and bottom panels correspond to results obtained in air and under low-pressure conditions (14 Pa), respectively. In air, desorption of water and hydroxyl groups from surfaces occurs at 50 and 480°C, respectively. Under low-pressure conditions, the drop in the weight ratio becomes larger and shifts by approximately 50°C to lower temperatures.

However, some features appear in the DTG curves that are not common for Cs- and K-saturated samples. The broad dip around 750 to 800°C for Cs-saturated vermiculite and the dip around 540°C for K-saturated vermiculite occur only under low-pressure conditions. If these features result from thermal decomposition of vermiculite, they would be observed in both samples. Thus, we attribute the dip around 750°C (540°C) in the bottom DTG curve in Fig. 2 (Fig. 3) to Cs (K) desorption.

Therefore, we used TDS to study Cs desorption from Cs-saturated vermiculite. The solid and dashed curves in Fig. 4

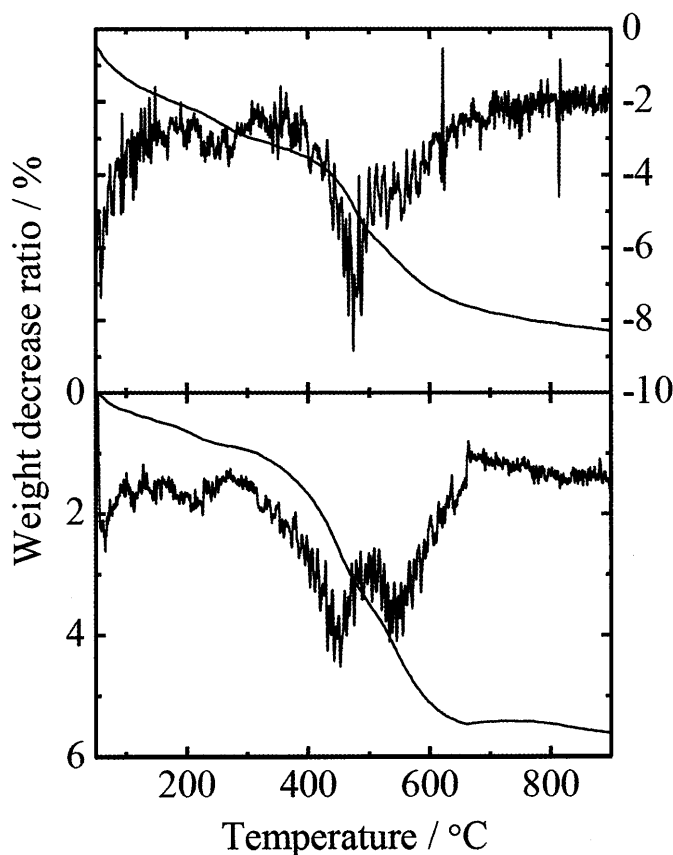


FIG. 3. TG and DTG curves of K-saturated vermiculite. Top and bottom panels correspond to the results obtained with sample in air and under low-pressure conditions (14 Pa).

are the TD and background spectra, respectively, of ^{133}Cs . These results show that desorption of Cs begins above 520°C and peaks around 660°C. We consider that the difference in pressure explains why the temperature of the thermal desorption peak does not coincide with the temperature of the drop in weight ratio in Fig. 2. The pressure for the TG measurement was 14 Pa, whereas that for the TDS measurement was less than 1×10^{-3} Pa. Thus, the Cs desorption temperature decreases with decreasing pressure.

Next, we discuss the amount of Cs that remains in the vermiculite after vacuum heat treatment. The right and left panels in Fig. 5 show, respectively, the Cs $3d_{3/2}$ and Si $1s$ XP spectra acquired using 3 keV X-rays. From top to bottom, the spectra correspond to the results at room temperature, 400, 600, and 800°C. Determination of the binding energies of these photoelectrons was made difficult by the space charge effect that arose because of the insulating property of clay minerals. Thus, we show kinetic energy on the horizontal axes in Fig. 5 instead of binding energy. Based on the results shown in Fig. 5, we calculated the intensity ratio $R = I_{\text{Cs}}/I_{\text{Si}}$, where I_{Cs} and I_{Si} are areas of the Cs $3d_{3/2}$ and Si $1s$ peaks, respectively. Figure 6 shows the ratio R/R_0 (R_0 was obtained at room temperature) as a function of temperature. Compared with the result at room temperature, the ratio R/R_0 decreases by 25% at 600°C and by 37% at 800°C, which suggests that Cs desorption from the clay minerals is more effective with increasing temperature. Although Cs does not desorb from Cs-saturated vermiculite in air (see Fig. 2), approximately 40% of the Cs was removed by heat treatment at 800°C under high-vacuum conditions. This indicates that low-pressure sublimation is useful for Cs decontamination of soil.

Furthermore, we acquired the TD spectrum of Cs-saturated vermiculite with NaCl-CaCl₂ mixed salt added at a 1/1 molar ratio. The weight ratio of salt to vermiculite was 1/10. Figure 7 shows the TD (solid line) and background (dotted line) spectra of ^{133}Cs scaled up by a factor of seven. The increase in both the TD and background spectra above 600°C is attributed to desorption of contaminant Cs from the wall of the alumina

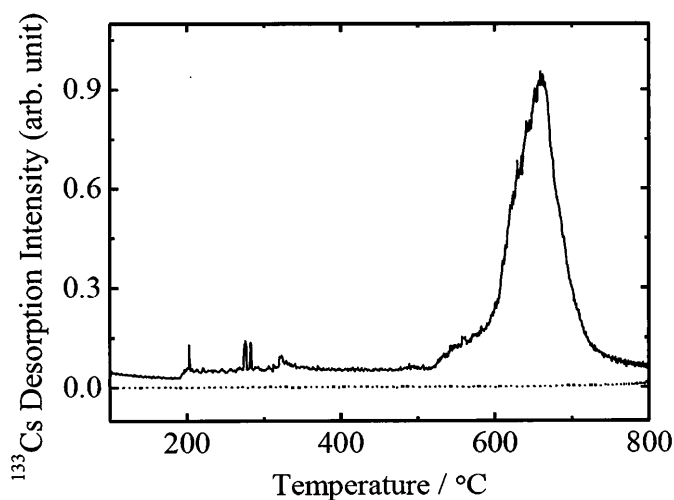


FIG. 4. Solid curve represents TDS spectrum of ^{133}Cs for Cs-saturated vermiculite. Dotted line represents background spectrum measured after TDS spectrum measurement.

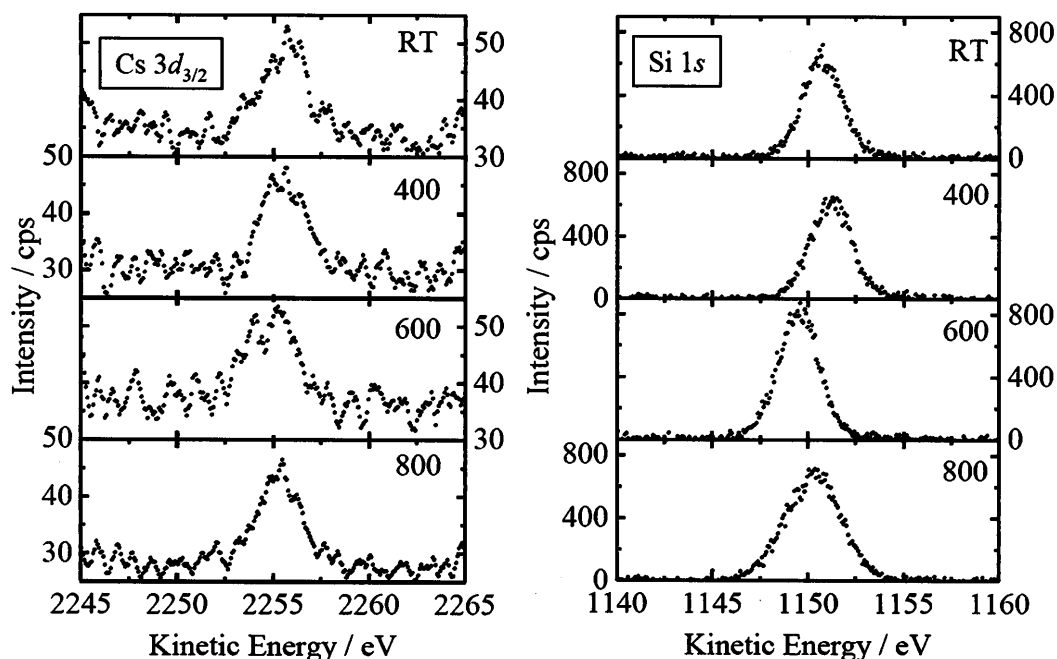


FIG. 5. Left and right panels show $Cs\ 3d_{3/2}$ and $Si\ 1s$ XP spectra, respectively, of vacuum-heated Cs-saturated vermiculite. Temperature is shown on the right side of each panel, and RT denotes "room temperature."

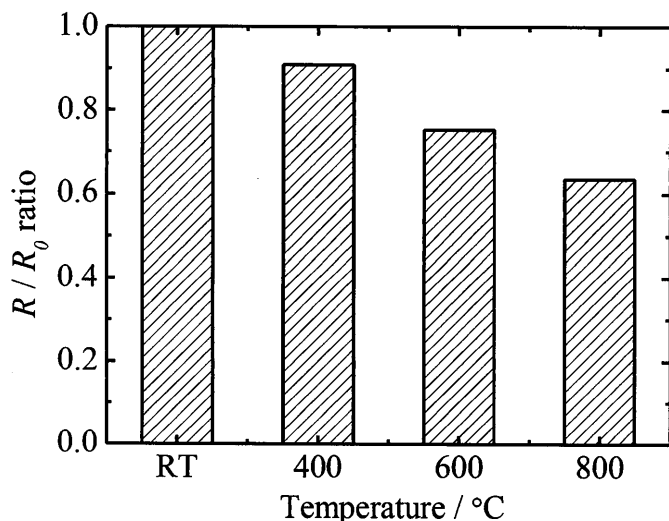


FIG. 6. Change in photoelectron peak intensity ratio R for $Cs\ 3d_{3/2}$ to $Si\ 1s$ derived from the results shown in Fig. 5. R_0 is the ratio for Cs-saturated vermiculite before heating.

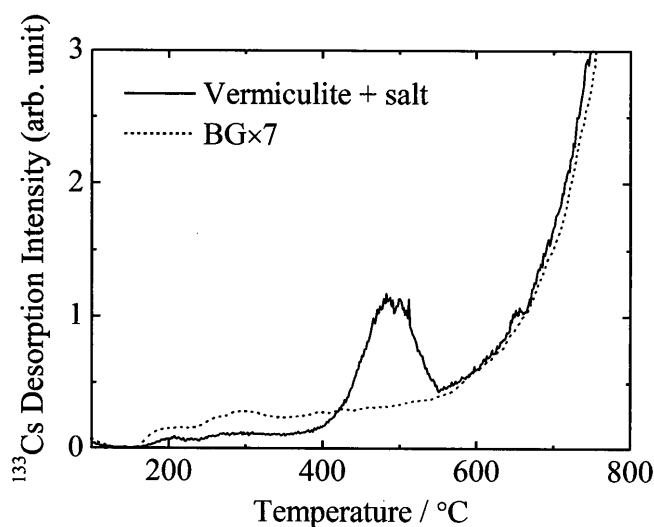


FIG. 7. Solid curve represents TDS spectrum of ^{133}Cs for Cs-saturated vermiculite with added NaCl-CaCl₂ mixed salts. Dotted line represents background spectrum scaled up by a factor of seven.

crucible. For samples with no added salt, the increase in the background above 600°C is very small, as shown in Fig. 4. This result indicates that the background intensity depends on the amount of mixed salt in the crucible, which suggests that the significant decrease in background intensity for salt-free samples with respect to that for salt-added samples (cf. dotted line in Fig. 4 vs dotted line in Fig. 7) is due to desorption of most of the salts during acquisition of the TD spectrum. Therefore, we consider herein that only the peak near 480°C is derived from the vermiculite. This peak shifts 180°C to lower temperatures with respect to the peak shown in Fig. 4; this indicates that the temperature of Cs desorption from clay

minerals can be significantly decreased using low-pressure sublimation and by adding salts.

We used XPS to determine the amount of Cs remaining in the sample with added salts. In this measurement, we added the mixed salt NaCl-CaCl₂ at the molar ratio of 1/2 to Cs-saturated vermiculite with a weight ratio of 1/1. Figure 8 shows $Cs\ 3d$ XP spectra acquired using an Al $K\alpha$ X-ray source. The top panel shows the result for the unheated sample with no salt and the bottom panel shows the result for the sample with added salt and maintained at 650°C for 30 min under low-pressure conditions (14 Pa). The horizontal axis represents the photoelectron kinetic energy and the vertical

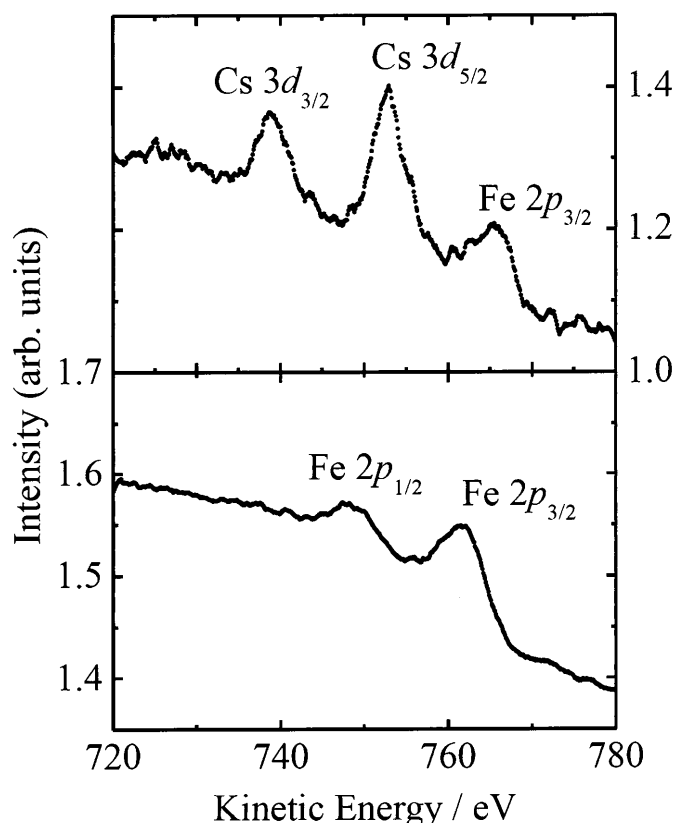


FIG. 8. Cs 3d and Fe 2p XP spectra of Cs-saturated vermiculite for photoelectrons ejected by Al $K\alpha$ X-rays. Top panel shows the result for a heated sample with no added salt. Bottom panel shows the result for a sample with NaCl-CaCl₂ added and maintained at 650°C for 30 min under low-pressure conditions (14 Pa).

axis represents the intensity normalized by the intensity of Si 2p peak. The three peaks in the XP spectrum of the unheated sample are assigned to Cs 3d_{3/2}, Cs 3d_{5/2}, and Fe 2p_{3/2} photoelectrons, respectively. Note, however, that the Fe 2p_{1/2} peak overlaps the Cs 3d_{5/2} peak. The Fe 2p_{1/2} and Fe 2p_{3/2} peaks appear in the XP spectrum of the heated sample, whereas the Cs 3d_{3/2} peak essentially disappears. This result indicates that the Cs content of the vermiculite is below the detection limit of XPS.

The inelastic mean free path of Cs 3d photoelectrons ejected from SiO₂ or Al₂O₃ by Al $K\alpha$ (3 keV) X-rays is less than 3 (5.5) nm (Tanuma et al., 1988). Thus, the XPS measurements performed for the present study only detected photoelectrons near the surface of the clay minerals, which took the form of particles ranging in size from 1.2 to 1.8 μ m. Confirming whether Cs sorbed in the bulk of the particles can be removed by the proposed method thus requires a more bulk-sensitive technique than XPS. However, the present results do indicate that the combination of low-pressure sublimation and adding salt has potential for Cs decontamination at lower temperatures than currently required by conventional dry methods.

CONCLUSION

Vermiculite particles from Fukushima were saturated and sorbed by nonradioactive Cs and heated in air and under

vacuum and low-pressure conditions. Comparing DTG curves shows that the weight decrease above 750°C observed when the samples are heated under low-pressure conditions (14 Pa) does not occur when the samples are heated in air. On the basis of the Cs desorption peak observed around 660°C in TD spectra acquired with the samples in vacuum, we attribute the mass decrease above 750°C in the low-pressure DTG curve to Cs desorption. XPS measurements clarify that approximately 40% of Cs is desorbed from vermiculite by vacuum heat treatment at 800°C for 3 min. These results demonstrate that the proposed low-pressure sublimation method is useful for removing Cs, which is only marginally removed by heating in air. Furthermore, TDS measurements indicate that adding a mixture of NaCl and CaCl₂ salt decreases the Cs desorption temperature by 180°C. Under low-pressure conditions (14 Pa), we confirm that the Cs XPS peak almost disappears upon maintaining Cs-saturated vermiculite with added NaCl and CaCl₂ salts at 650°C for 30 min. These results show the effectiveness of Cs decontamination by the proposed dry method, which combines low-pressure sublimation and the addition of mixed salts.

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